Characterization of Oxygen-rich Ti$_2$AlC Thin Films

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In this Thesis Ti-Al-C thin films deposited by cathodic arc at 700, 800 and 900 °C were investigated with respect to composition, structure and mechanical properties. The highest growth temperature resulted in close to single crystalline Ti$_2$AlC MAX phase.

A high oxygen incorporation of 7-12 at.% was detected in all the films, likely originating from residual gas and the Al$_2$O$_3$ substrate. It was evident that the characteristic nanolaminated MAX phase structure was retained upon deflection from the ideal MAX phase stoichiometry.

Hardness and elastic modulus of the sample grown at 900 °C were 16 and 259 GPa, respectively, as determined by nanoindentation using a Berkovich tip. Nanoindentation measurements with a cube corner tip were also performed on all three samples in order to extract elastic moduli.

Analysis of loading-unloading curves and SPM images revealed no relation between pop-in events and pile-ups around the residual imprints, indicating that other mechanisms than formation of kink bands may be responsible for formation of pile-ups. This was also confirmed by cross-sectional TEM investigation of an indent: Ti$_2$AlC MAX phase deformed without kinking and delamination, as opposed to the observations in single crystalline Ti$_3$SiC$_2$ films. Several possible reasons for the different deformation mechanism observed are discussed.

These results are of importance for the fundamental understanding of the origin of material characteristics, and serve as an initial study initiating further investigations of the influence of defects on MAX phase properties.
Abstract

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These results are of importance for the fundamental understanding of the origin of material characteristics, and serve as an initial study initiating further investigations of the influence of defects on MAX phase properties.
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1 Introduction

Materials science is an interdisciplinary field involving the study of properties of materials and how those are determined by composition and (micro-)structure. Understanding these relations offers the possibility to design new materials with improved properties. Manipulation of defects, such as substitutional and interstitial atoms, vacancies, grain size, and inclusions of other phases, is a common approach to tune properties such as, e.g., hardness, oxidation resistance, thermal stability, and resistivity.

This work concerns the relation between composition, structure and materials properties of thin films, with model system as presented below. Thin film synthesis involves deposition of a thin layer of material (coating) onto another material (substrate) in order to achieve properties that can not be attained by the substrate or coating material alone.

The materials in focus of this Thesis are MAX phases (M denotes an early transition metal, A – an A-group element, and X – carbon or nitrogen) with the general composition of $M_{N+1}AX_N$. These phases form a family of nanolaminated ternary carbides and nitrides. The first members in this group were discovered in 1960’s by Jeitschko and Nowotny.[1,2] However, interest in MAX phases arose again in mid 1990’s when Barsoum et al. synthesized bulk $Ti_3SiC_2$ and reported its remarkable metal/ceramic-like as well as favourable mechanical properties.[3]

~60 MAX phases have been synthesized in polycrystalline bulk form to date. Deposition of thin films is, however, less extensive due to a more recent research activity in the field. While most of the investigations concentrate on establishing growth conditions leading to single crystalline films and their subsequent characterization, only a few studies have been reported which focus on the influence of structural defects on the MAX material’s properties, see for example Ref. 4. Studies focusing on impurity incorporation in MAX phases are even more scarce, and only recently substantial oxygen incorporation in $Ti_2AlC$ was reported.[5,6] Incorporation of impurities is, however, a very important issue, since it may affect the material’s performance. Increasing the fundamental understanding of the correlation impurity – properties also offers the possibility to tailor the already unique MAX phase properties by intentional introduction of various elements.

1.1 Objectives

The purpose with this Thesis is to investigate the mechanical properties and deformation mechanisms of arc deposited $Ti_2AlC$ with ~10% oxygen incorporated into the characteristic MAX phase structure. Hardness, elastic modulus, and deformation upon indentation is evaluated, and compared to what is available in the literature for both “pure” $Ti_2AlC$ and other MAX phase materials.
2 MAX phases

2.1 Crystal structure

The elements forming MAX phases are highlighted in a periodic table in Figure 2.1, where the elements marked with red, blue and black correspond to early transition metals, A-group elements, and carbon/nitrogen, respectively.

Figure 2.1. Periodic table illustrating elements forming MAX phases.

These elements form a characteristic hexagonal crystal structure also described as M₆X edge sharing octahedra interleaved with single layers of A-elements. The general composition can be written Mₙ₊₁AXₙ (n = 1-3), where the different stoichiometries are referred to as 211 (M₂AX, e.g., Ti₂AlC, Ti₂AlN), 312 (M₃AX₂, e.g., Ti₃AlC₂, Ti₃SiC₂) and 413 (M₄AX₃, e.g., Ti₄AlN₃, Ti₄SiC₃, Ti₄GeC₃, Ta₄AlC₃). The corresponding unit cells are shown in Figure 2.2.

Figure 2.2. Unit cells of a) 211, b) 312 and c) 413 MAX phases.[7]
2.2 Material properties

MAX phases are very intriguing since they exhibit a combination of properties characteristic for both ceramics and metals: they are hard, wear- and oxidation resistant (ceramic-like), in combination with being good electrical and thermal conductors (metal-like). This stems from the presence of two types of atomic bonding: metallic M-A bonds and ionic-covalent M-X bonds.

Furthermore, the nanolaminated structure in combination with weak M-A bonds allows easy sliding of basal planes (MX and A layers) when shear stress is applied, leading to machinability (can be cut with a hacksaw) and extreme damage tolerance.

To complete the list of exiting and inspiring properties of MAX phases, it should be added that these compounds are thermodynamically stable at high temperatures (some as high as 2300 °C) and can withstand drastic temperature changes (“thermal shock”).

All these characteristics make MAX phases attractive for many industrial applications, e.g., high temperature components, sliding electrical contacts, wear protective and lubricant coatings, and corrosion resistant coatings.

2.3 Deformation mechanism

Materials showing anisotropy in shear strength, e.g., materials with hexagonal crystal lattice (when c/a ≥ 1.73 [8]), deform by formation of kink bands when loaded parallel to the weak shear planes (also referred to as “basal planes”).

When the shear stress is high enough, pairs of dislocations of opposite sign are created. Dislocations move along shear planes in opposite directions and arrange themselves in two dislocation walls, severely changing the direction of the parallel shear planes, i.e., creating a “kink”, with an undisturbed crystal lattice in between, so called “kink band”.

A sketch of a kink band formation is presented in Figure 2.3.

![Figure 2.3. Kink band formation: a) Edge dislocations (denoted as ) of opposite sign move in opposite directions. b) Dislocations are arranged in two dislocation walls forming kink boundaries with a kink band in between.[7]](image-url)
When the load is high enough, basal planes separate from each other forming delaminations.

It is popular to explain kinking in analogy with a deck of cards, the cards representing basal planes. When force is applied on the deck sides, the cards easily slide on top of each other (low shear strength), then bend irreversibly (“kink”) and separate (“delaminate”), as shown in Figure 2.4.

![Figure 2.4. Kinking analogy with a deck of cards.][9]

Studies on deformation mechanisms of MAX phases mainly involve investigations of Ti₃SiC₂ (c/a = 5.76) in polycrystalline bulk form [9] and as single crystalline thin films.[10] Formation of kink bands has been observed in both cases. This is, however, not enough to claim that all MAX phases deform by kinking, especially if defects are presented in the structure.

### 2.4 Ti₂AlC

The MAX phase thin films in focus of this Thesis is Ti₂AlC. A schematic picture of the crystal unit cell is shown in Figure 2.5a, with cell parameters of \( a = 3.04 \) Å and \( c = 13.60 \) Å.

A phase diagram of the Ti-Al-C system at 1000 °C is presented in Figure 2.5b. Apart from Ti₂AlC there exist two more stable ternary phases: Ti₃AlC₂ (312 MAX phase) and Ti₃AlC (perovskite).

![Figure 2.5. a) Unit cell of Ti₂AlC.[11] b) Phase diagram of the Ti-Al-C system at 1000 °C. Partly redrawn from.[12]
Ti$_2$AlC exhibits an interesting property to form a layer of $\alpha$-Al$_2$O$_3$ at high temperatures which prevents its further oxidation. Due to very similar thermal expansion coefficients and good adhesion of $\alpha$-Al$_2$O$_3$ layer, thermal cycling is possible. This is one reason why Ti$_2$AlC has gained particular interest from industry, with potential applications of, e.g., heating elements and gas burner nozzles.

The mechanical properties of Ti$_2$AlC have been investigated both theoretically and experimentally: Sun et al. reported a bulk Ti$_2$AlC elastic modulus of 304.8 GPa derived by \textit{ab initio} calculations.[13] Wilhelmsson et al. investigated mechanical properties of magnetron sputtered Ti$_2$AlC thin films (thickness = 600 nm) by nanoindentation.[14] Hardness of 20±1 and ~15 GPa as well as reduced elastic modulus of 260±10 and ~240 GPa were reported for shallow and deep indents, respectively.

The deformation mechanism of polycrystalline Ti$_2$AlC have been studied by Zhou and Wang [11] and Zhou et al.[15] At room temperature, the deformation primarily occurred by kinking, delamination of nanolaminated grains, and formation of voids and cavities. However, no studies are published on deformation behaviour of Ti$_2$AlC \textit{single crystalline} material.

Recently, evidence of substantial O incorporation in arc deposited Ti$_2$AlC thin films was presented, the oxygen likely originating from residual gas [5] as well as from the Al$_2$O$_3$ substrate.[6] It was indicated, that O takes C lattice positions. Despite high O content, the characteristic nanolaminated structure was retained, and calculations show a maximum decrease in cell parameters of 1.2 % upon O incorporation up to 18.75 at.%. [5] To date, there are no experimental or theoretical investigations reported on the effect of O impurities on the materials properties.
3 Thin film synthesis

Thin film synthesis techniques are divided into two main groups: chemical vapour deposition (CVD) and physical vapour deposition (PVD). In CVD, thin films are deposited through gas phase reactions. Consequently, a high temperature is required, which limits the choice of substrate material. PVD processes, on the other hand, involve condensation of growth species from plasma. The substrate temperature may therefore be considerably lower.

Bulk synthesis techniques, such as hot isostatic pressing, and CVD have been the primary methods to synthesize MAX phase material as bulk and thin films, respectively. However, using CVD it is difficult to grow pure single crystal material due to gas phase depletion and HCl etching.

Magnetron sputtering is an approach belonging to PVD methods, and so far the most successful synthesis technique of thin MAX phase films, see for example Ref. 16 and 17. There have also been attempts to use pulsed laser deposition (PLD) for Ti$_3$SiC$_2$ thin film synthesis.[18] Although no unambiguous evidence of MAX phase has been reported, PLD still demonstrates potential due to production of highly energetic species, and could possibly be an alternative method for sputtering in the future.

A new promising method for MAX phase synthesis, cathodic arc deposition, has recently been reported by Rosén et al.[19] Ti$_2$AlC thin films investigated in this Thesis were grown by the latter technique at Sydney University.

3.1 Cathodic arc

In cathodic arc, a discharge is generated between anode and cathode (target) and a molten pool, called arc spot, is created, from which cathode material is evaporated and electrons are emitted. The electrons are accelerated by an electric field, collide with and ionize the evaporated atoms. The resulting plasma has a high degree of ionization (close to 100%), including presence of multiply charged ions, with inherent high ion energies. A high ionization degree is advantageous through the availability to manipulate the plasma by electric or magnetic fields. This is beneficial in terms of process control, and allows deposition of stable as well as metastable phases.

During plasma generation there is co-emission of cathode material in the form of microdroplets. These adhere to the growing film, which results in lower crystalline quality, non-uniform composition and rough surface. To suppress droplet formation and hinder their arrival to the growth zone, reduction (steered arc, pulsed arc) or removal (shaded arc, filtered arc) techniques are used, respectively. A combination of these techniques is also common.

3.1.1 Experimental details of thin film synthesis

The Ti$_2$AlC thin films were deposited using high current (900 A) pulsed cathodic arc at a base pressure of 1×10$^{-6}$ mbar. Three cathodes of Ti, Al and C, see Figure 3.1a, were used in
alternating mode at a frequency of 10 Hz. The ratio of pulses from the different cathodes was 15 Ti to 1 C to 10 Al.

A curved magnetic filter was employed to remove microdroplets from the plasma plume. The magnetic field guides the electrons towards the substrate, whereas the ions follow the electrons due to Coulomb attraction and the constraint of a quasineutral plasma. Neutral microdroplets, on the other hand, continue their straight motion towards the chamber walls. A schematic representation of the deposition system is shown in Figure 3.1b.

Prior to deposition, sapphire (0001) substrates were rinsed in ethanol and degassed in the vacuum chamber at 900 ºC for 5 min in order to get rid of surface contamination.

Initially, ~10 nm Ti and ~10 nm TiC$_{0.75}$ (111) layers were deposited to gradually match the Ti$_2$AlC lattice and initiate strain-free epitaxial (0001) MAX phase growth.

Thin films were deposited at three different substrate temperatures: 700, 800 and 900 ºC, with a resulting thickness of 360, 290 and 480 nm, respectively. Labeled after the growth temperature, the samples are referred to as Film700, Film800 and Film900 later in the Thesis.
4 Materials characterization

4.1 Elastic recoil detection analysis (ERDA)

Elastic recoil detection analysis (ERDA) enables reference-free determination of elemental composition including depth profiling. A beam of highly energetic ions is directed towards a sample at a low angle \( \alpha \) (10-15º), see Figure 4.1. The beam causes sample atoms to recoil at energies depending on their mass. In order to suppress background of scattered incident ions, a filter is placed in front of the detector.

\[ E_r = 4E_i \frac{m_im_r}{m_i + m_r} \cos^2 \theta \]  

**Equation 4.1**

The energy of the incident ions is known, and the scattering angle as well as the energy of the recoiled atoms is measured. Hence, the mass of the atoms presented in the sample can easily be calculated from a simple elastic interaction equation:

\( E_r \) – energy of a recoiled atom  
\( E_i \) – energy of an incident ion  
\( m_i \) – mass of an incident ion  
\( m_r \) – mass of a recoiled atom  
\( \theta \) – scattering angle

Since the atomic mass is characteristic for each element, an elemental composition of the sample can be determined.

ERDA is mostly used to detect light elements, including hydrogen, which is rather difficult to quantify with standard analytical laboratory equipment. Heavy elements do not recoil easily and their energies tend to overlap with energies of the backscattered incident ions. Rutherford backscattering spectroscopy (RBS) is another ion beam analysis technique, more suitable for detection of heavy atoms.
4.1.1 Experimental details of ERDA

ERDA measurements of the thin films were performed in Tandem laboratory at Uppsala University. An $^{127}$I$^{+}$ ion beam accelerated to 40 MeV hit the sample surface at incidence angle of 67.5° ($\alpha = 22.5^\circ$). The recoiled atoms were detected at scattering angle of 45°. Data obtained was evaluated using the CONTES code.[20]

4.2 Nanoindentation

4.2.1 Hardness and elastic modulus

The most important parameters reflecting material’s mechanical properties are hardness H and elastic modulus E (also referred to as Young’s modulus). Both hardness and elastic modulus are determined by examining material’s response to applied load. Materials deform in two ways: elastically (atomic bonds stretch but do not break, i.e., reversible deformation) while the load is low and, at higher loads, plastically (bonds break, there is generation and propagation of dislocations, i.e., permanent deformation).

Elastic modulus is related to elastic deformation and measures material’s ability to withstand changes in length, which in turn depends on bond stiffness (i.e., “bond strength”).

Hardness is material’s property to resist plastic deformation.

4.2.2 Introduction to nanoindentation

Nanoindentation is used to determine the hardness and elastic modulus of thin films, including effects of, for example, modified surface layers, and grains of different phases.

![Figure 4.2. a) Load-displacement curve. b) Cross-section through an indent.[21](P_{\text{max}} - \text{maximum load}, h_r - \text{residual depth}, h_e - \text{elastic depth}, h_c - \text{contact depth}, h_a - \text{depth of circle of contact}, h_{\text{max}} - \text{maximum depth}, \frac{dP}{dh} - \text{contact stiffness}, a - \text{radius of circle of contact})]
While an indenter is pressed into the material’s surface, the applied load and displacement are continuously recorded. A typical load-displacement curve, as well as a cross section through an indent, is shown in Figure 4.2.

Typically, elastic-plastic loading is followed by elastic unloading (elastic strains relax and material partly recovers). The residual depth of an indent is determined by the amount of plastic deformation.

It should be pointed out that contact depth is not equal to maximum penetration depth. The material’s surface rarely remains flat around the indenter tip. Surface behaviour characteristic for ceramics (sink-in) and metals (pile-up) is shown in Figure 4.3.

![Figure 4.3. Sink-in (left) and pile up (right) behaviour resulting from indentation.][21]

MAX phases exhibit unique behaviour, as they are ductile ceramics and therefore pile-up.

Nanoindenter tips are usually fabricated from diamond due to its exceptional stiffness (E = 1141 GPa) and hardness (H = 100 GPa). Several tip geometries are available, the three-sided pyramid Berkovich tip, see Figure 4.4, being the most common.

![Figure 4.4. Berkovich indenter tip: a) schematic of three-sided pyramid geometry, h_c – contact depth, \( A_{pr,c} \) – projected contact area [21] and b) scanning electron microscope image.][21]

4.2.3 Oliver and Pharr method

Nanoindentation enables extraction of a reduced elastic modulus \( E_r \), which depends on both sample (in the case of thin film: thin film and substrate) and indenter tip properties, and is expressed as
\[ E_r = \frac{1}{2} \frac{\pi}{A_{pr,c}} \left( \frac{dP}{dh} \right)_{P=P_{\text{max}}} \]  

Equation 4.2

where \( A_{pr,c} \) is the projected contact area.

The hardness, in turn, is expressed as

\[ H = \frac{P_{\text{max}}}{A_{pr,c}} \]  

Equation 4.3

Oliver and Pharr demonstrated that a power law fit is the best approximation of the unloading curve:[22]

\[ P = a \cdot (h - h_c)^m \]  

Equation 4.4

\( a \) – constant

\( m \) – power law index, within a range \([1.1; 1.8]\), depending on the material

\( h \) – penetration depth

The projected area of contact is determined indirectly, using the known geometry of the indenter tip. For a Berkovich tip the projected contact area is written as

\[ A_{pr,c} = 3\sqrt{3}h_c^2 \tan \theta = 24.5h_c^2 \]  

Equation 4.5

where \( \theta = 65.3^\circ \).

\( h_c \) is found from

\[ h_c = h_{\text{max}} - \frac{\varepsilon \cdot P_{\text{max}}}{(dP/\text{dh})_{P=P_{\text{max}}}} \]  

Equation 4.6

\( \varepsilon \) – indenter shape constant

\( \varepsilon = 0.72 \) for Berkovich indenter

### 4.2.4 Nanoindenter tip area function

The shape of a real indenter tip, even if new, deviates from the ideal shape (an ideal tip is infinitely sharp). Use of the ideal \( A_{pr,c} \) vs. \( h_c \) relation (Equation 4.5) leads to substantial errors, especially at small penetration depths, as demonstrated in Figure 4.5.
Calibration, i.e., a series of indentations into a standard material must be performed to establish the actual indenter area function $A_{pr,c}(h_c)$.

$$A_{pr,c} = 24.5 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + ...$$

Equation 4.7

$C_1, C_2, C_3, ...$ - correction terms

Typically, fused silica is used for calibration, with $E = 72.5$ GPa and $H = 8-10$ GPa.

### 4.2.5 Nanoindentation of thin films

Characterization of thin film properties is of high importance, even when corresponding bulk material is well investigated. Thin film and bulk material are often different in terms of quality of crystal structure, presence and concentrations of impurities, internal stress, etc., which lead to substantial differences in their properties. For example, the hardness of bulk Ti$_3$SiC$_2$ is 5 GPa,[7] while the reported value for the corresponding thin film is 24 GPa.[23]

Nanoindentation enables measurement of mechanical properties of thin films without removing them from the substrate. Care must be therefore taken to avoid substrate influence, especially when determining the film hardness.

Bückerle rule which restricts the maximum penetration depth to 10% of the film thickness is commonly applied as a guideline to avoid undesirable substrate influence on the measurement. However, the film must be thick enough to allow undisturbed formation of the fully-developed plastic zone (plastic zone – region beneath the surface where plastic
deformation is created). This is equivalent to the mean contact pressure $p_m$ ($p_m = \frac{P_{\text{max}}}{A_{\text{pr.c}}}$) being constant even if the load is further increased. If the film is too thin, the plastic zone extends to the substrate and obtained results are affected by the substrate’s properties. For the same reason probing of hard films on soft substrates should always be avoided since the plastic zone easily crosses the film-substrate interface.

Use of a Berkovich tip is suitable for a film thickness of more than $\sim 300 \text{ nm}$. The lower limit of the thickness arises from the fact that a real tip has a radius, initially typically 50-150 nm. As the tip is used, especially for extensive measurements on hard materials, it becomes blunter, to a radius of $\sim 300 \text{ nm}$. Therefore, for probing of thinner films of thickness in the range 50-300 nm, a sharper ($\theta = 35.26^\circ$) cube corner tip is preferred, see Figure 4.6. The tip enables creation of plastic deformation at smaller penetration depths, thus reducing substrate effects.

![Figure 4.6. Cube corner indenter tip.][21]

The most common and reliable method to determine the film hardness is to perform a series of indentations at various loads corresponding to a maximum penetration depth of $\sim 5 - 20\%$ of the film thickness. For evaluation the dependence $p_m$ vs. $h_{\text{max}}$ is then plotted, see Figure 4.7.

![Figure 4.7. Typical $p_m$ vs. $h_{\text{max}}$ dependence for a soft film on a hard substrate.][22]

Region I illustrates development of the plastic zone with increasing load, i.e., increase in $p_m$.

Region II is used to determine the film’s hardness: the plastic zone has fully developed and is all accommodated in the film, i.e., $p_m = \text{const.}$
In region III, influence from the substrate is more and more pronounced as the load increases, since the fully-developed plastic zone extends into the substrate, resulting in increase in hardness (in the case of a soft film on a hard substrate).

If no plateau (region II) is observed, the film is apparently too thin to accommodate the fully-developed plastic zone, i.e., region III follows directly after region I.

It should be noted that hardness, in contrast to elastic modulus, is not an intrinsic material’s property, i.e., hardness is affected by microstructure (grain size and boundaries, precipitates, inclusions, voids, etc.), loading orientation (for anisotropic materials), and environment (temperature, humidity, etc.). Hardness should therefore always be evaluated using a statistical approach.

The analysis procedure is different when measuring the elastic modulus of the film, since any indentation results in elastic deformation of both the film and substrate. To determine the elastic modulus, a series of indentations from low to high load is performed (the “10 % rule” is no longer valid). The dependence $E_r$ vs. $h_{\text{max}}$ is then plotted and data extrapolated back to zero depth, as shown in Figure 4.8, in this way excluding substrate influence. However, the resulting value of $E_{r0}$ corresponds to a value for the film-indenter system, including possible tip deformation. Taking these effects into account is reasonable, considering that materials with $E = 300$-400 GPa (i.e. 25-30 % of the value for diamond) are quite commonly tested. The following formula is used to account for influence from the indenter:

$$\frac{1}{E_{r0}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}$$

Equation 4.8

$E_{r0}$ – reduced elastic modulus at $h_{\text{max}} = 0$
$E$ – thin film’s elastic modulus
$\nu$ – thin film’s Poisson’s ratio
$E_i$ – indenter’s elastic modulus
$\nu_i$ – indenter’s Poisson’s ratio

Figure 4.8. Dependence $E_r$ vs. $h_{\text{max}}$. Extrapolation to zero depth gives elastic modulus $E_{r0}$ of film-indenter system.
4.2.6 Experimental details of nanoindentation

Hardness and elastic modulus measurements

Nanoindentation was performed at room temperature using a Hysitron Triboscope nanoindenter. Prior to the tests, the samples were mounted in the environmental enclosure for 0.5-2 h to reach thermal equilibrium. The Oliver and Pharr method was used for data analysis, including fitting of 75% of the unloading curve.

The thickest film (Film900, ~480 nm) was characterized with a Berkovich indenter tip. Indentations with maximum load of 200-9000 µN were made, corresponding to 20-150 nm maximum penetration depth (4-30% of the film thickness). The profile of the applied load is shown in Figure 4.9a. A series of measurements were made on different occasions to account for possible environmental effects, such as temperature fluctuations, humidity, etc.

![Figure 4.9](image)

**Figure 4.9.** The sequence of applied load for a) Film900 analyzed with a Berkovich tip and b) Film900, Film800 and Film700 analyzed with a cube corner tip.

A cube corner tip was employed in order to induce more plastic deformation than what is possible with a Berkovich tip. A maximum load of 150–2000 µN was applied. The loading profile is depicted in Figure 4.9b; the loading time was varied between 5 and 200 s in order to observe loading rate influence (5-300 µN/s) on the curve shape. Holding segment at 0.1P<sub>max</sub> load was introduced to detect any thermal drift.

The Film700 and Film800 were characterized with a cube corner tip, with an indentation sequence as shown in Figure 4.9b. The loading time was varied between 10 and 30 s.

**Indents for transmission electron microscopy analysis**

In order to identify the deformation mechanism in the material, cross-sectional transmission electron microscopy of an indent was used. In preparation, a line of 5 indents with loads from 20 to 30 mN was made with a UMIS nanoindenter equipped with a Berkovich tip. The loading rate was ~400 µN/s. The indent made at P<sub>max</sub> = 24 mN was later selected for the analysis.

4.3 Transmission electron microscopy (TEM)

The transmission electron microscope (TEM) is an invaluable analysis tool for materials investigation on the nanoscale.
The working principle of a TEM is very similar to that of a conventional optical microscope. The main difference lies in replacing visible light (photons) with a beam of electrons, and, obviously, using electromagnetic lenses instead of the optical ones.

The de Broglie wavelength of highly energetic electrons (e.g., acceleration voltage of 200 kV corresponds to $\lambda_{\text{de Broglie}} = 2.5 \text{ pm}$) is significantly smaller than the wavelength of the visible light (400-750 nm). This leads to much greater point resolution (down to 2 Å), enabling investigation of sample features at the atomic level.

Interaction between an electron beam and a sample is not trivial, involving transmission, absorption, diffraction, scattering, emission of Auger and secondary electrons, generation of X-rays, etc. Transmission and scattering are the most important contrast providing events. Sample areas with different characteristics, e.g., composition, phases, crystal plane orientations, defects, stress field, etc., acquire different levels of the grayscale due to different electron scattering abilities.

Electron transparency is required for TEM investigation, which means sample thickness of ~100 nm or less. This can be achieved by e.g., cleaving, mechanical grinding followed by ion milling, focused ion beam milling, etc.

**4.3.1 Focused ion beam (FIB) milling**

Focused ion beam (FIB) milling is the only TEM sample preparation technique which enables precise selection of a desired sample area for analysis, e.g., an indent, as required for the work of this Thesis.

An accelerated ion beam, typically Ga$^+$ at 5-50 keV, is directed towards the sample to mill ~10 µm depth trenches from both sides of the area of interest, leaving a ~1 µm thin-window in between, see Figure 4.10.

![Figure 4.10](image.png)

**Figure 4.10.** a) Schematic representation of FIB sample preparation (not to scale) and b) thin-window in the Film900 depicted by scanning electron microscopy.

To reduce ion damage, the area of interest is covered by ~1 µm Pt layer prior to the FIB milling procedure. This is typically done by FIB-assisted chemical vapor deposition. An organometallic gas is introduced into the vacuum chamber with resulting chemisorption
onto the sample. An ion beam is scanned over the surface, thereby inducing decomposition of the gas molecules into volatile and non-volatile compounds, the latter being Pt.

The thin-window is then cut with the ion beam at the sides, welded to a micromanipulator needle, cut at the bottom, and transported to a Cu grid, where it is milled further to reach electron transparency.

**4.3.2 Experimental details of TEM and FIB**

The cross-section of an indent was studied using FEI Tecnai G² TF 20 microscope operating at 200 kV acceleration voltage.

The cross-sectional specimen for TEM analysis was prepared by Zeiss 1540 EsB Crossbeam FIB. A 30 keV Ga⁺ ion beam was used for milling.
5 Results

5.1 Composition

The elemental composition of the films was determined by ERDA, see Figure 5.1.

![Composition depth profile obtained by ERDA: a) Film700, b) Film800, c) Film900.](image)

As shown in the graphs, the content of Ti and Al is approximately homogeneous throughout the films. Correspondingly, no drastic changes are observed for C and O, however, a weak correlation between the C and O concentration is indicated in the Film900: as the C concentration increases, the O concentration decreases, especially evident from the depth profile in the region of 500-1000 a.u. (Figure 5.1c). Point-by-point analysis of the curves should, however, be done with care, due to possible instrumental errors.

The average film composition is shown in Table 1, where the composition close to sample surface and interface has been excluded from the calculations.

<table>
<thead>
<tr>
<th></th>
<th>Ti, at.%</th>
<th>Al, at.%</th>
<th>C, at.%</th>
<th>O, at.%</th>
<th>C and O, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film700</td>
<td>62</td>
<td>9</td>
<td>22</td>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>Film800</td>
<td>57</td>
<td>13</td>
<td>18</td>
<td>12</td>
<td>30</td>
</tr>
<tr>
<td>Film900</td>
<td>54</td>
<td>21</td>
<td>17</td>
<td>9</td>
<td>26</td>
</tr>
</tbody>
</table>

The analysis shows that the average Ti and Al concentration decreases and increases with increasing growth temperature, respectively. Correspondingly, a small decrease in the C content is also observed. The Ti:Al:C at.% of the Film900 is 54:21:17, which is closest to the stoichiometric Ti$_2$AlC values of 50:25:25. However, it is worth noting that the C and O content together correspond to 26 at.% in the Film900.

The Film700 and Film800 exhibit concentrations diverging from the ideal 211 MAX phase composition with too high Ti content and too low Al content; 57:13:18 and 62:9:22 at.%, respectively.

A high O incorporation (7-12 at.%) is observed in all the films, with an added average C and O content of ∼26-30 at.%. Concentrations of other impurities are below the detection limit.
**5.2 Structure**

In previous work, the structure of the films has been analyzed with x-ray diffraction (XRD).[24] For the present work, additional TEM analysis was performed.

Cross-sectional TEM analysis of the Film900 revealed the characteristic nanolaminated MAX phase structure, as exemplified in Figure 5.2.

![Cross-sectional TEM image of the Film900](image)

**Figure 5.2.** Cross-sectional TEM image of the Film900, showing the characteristic nanolaminated structure.

The XRD data [24] presented in Figure 5.3a confirms that at 900 °C the MAX phase grows epitaxially and that the hexagonal lattice structure is retained despite of high O concentration.

The film thickness is different for the three samples and it is therefore not possible to compare the relative peak intensities as an indication of the amount of corresponding phase in each sample. However, a comparison of phases present within one sample can be made.

For the sample deposited at 900 °C, more than 97 % of the integrated peak intensity can be attributed to Ti$_2$AlC {000x} type peaks (please note the logarithmic scale of the y-axis in Figure 5.3). The additional minor peaks at ~36° and ~76° originate from the seed layer and possible intergrown TiC.

As the growth temperature is decreased to 800 °C, a peak at ~38° indicating Ti$_3$AlC appears. There is also evidence of Ti$_2$AlC formation, though relative quantification via peak
integration is not possible due to peak overlapping. Comparing the intensity of the TiC peaks and the MAX phase peaks, it is evident that the fraction of TiC in the Film800 is higher than in the thicker Film900.

The Film700 consists primarily of TiC and Ti$_3$AlC, no Ti$_2$AlC is indicated.

![XRD θ-2θ scan](image)

**Figure 5.3.** XRD θ-2θ scan of a) Film900, b) Film800 and c) Film700. (The region of 40-44° is not shown to avoid the intense (0006) substrate peak).[24]

In Figure 5.4, images from scanning probe microscopy (SPM) are presented. Growth of cubic TiC is indicated in images from the Film700 (Figure 5.4a) as sparsely spaced pyramids of ~30-60 nm height. This is consistent with the presented XRD data. The surface of the Film800 also exhibits protrusions, however, not as regular in form. The surface of both films is rough, which possibly arises from many pyramids/protrusions in the early formation stages. No pyramids/protrusions are presented on the Film900.
5.3 Mechanical properties

5.3.1 Hardness

Hardness could only be determined for the thickest film, Film900 (~480 nm). The dependence $p_m$ vs. $h_{\text{max}}$ in Figure 5.5 corresponds well to Figure 4.7, with three different “zones”. The mean pressure $p_m$ is nearly constant for $h_{\text{max}} = 36-82$ nm (7-17 % of the film’s thickness) with a resulting average value of 16 GPa for the film hardness (standard deviation 0.6).
5.3.2 Elastic modulus

Poisson’s ratio \( \nu \) of thin films is typically in the range of 0.2-0.3. The average value of 0.25 was used in calculations to obtain elastic modulus \( E \) (Equation 4.8).

The dependence \( E_r \) vs. \( h_{\text{max}} \) for the Film900, obtained with a Berkovich tip, is presented in Figure 5.6. Data points with \( P > 3000 \, \mu N \) (\( h_{\text{max}} > 90 \, \text{nm} \)) were not included to avoid possible influence of pile-ups. The resulting value of \( E \) was calculated to 259 GPa.

![Figure 5.6.](image)

**Figure 5.6.** \( E_r \) vs. \( h_{\text{max}} \) for the Film900 obtained with a Berkovich tip (\( E_{\text{r0}} = 222 \, \text{GPa} \)).

Measurements with a cube corner tip were also performed, see Figure 5.7. Pile-ups were observed for \( P > 400 \, \mu N \) (all data points). The calculated value of \( E \) was then 214 GPa.

![Figure 5.7.](image)

**Figure 5.7.** \( E_r \) vs. \( h_{\text{max}} \) for the Film900 obtained with a cube corner tip (\( E_{\text{r0}} = 191 \, \text{GPa} \)).
Additional measurements were performed on the Film800 and Film700, see Figure 5.8 a) and b). A cube corner tip was used for all indents, with analysis and calculations resulting in E values of 246 and 282 GPa, respectively.

![Figure 5.8](image)

**Figure 5.8.** $E_r$ vs. $h_{max}$ for a) Film800 ($E_{r0} = 213$ GPa) and b) Film700 ($E_{r0} = 239$ GPa) obtained with a cube corner tip. Measurements made on two occasions are presented in (b), illustrating similar scattering of data points independent on the sample area chosen for indentation.

The scattering of data points increases with decreasing growth temperature, as the surface is rougher and more Ti$_3$AlC and TiC grains are present.
5.4 Materials deformation

5.4.1 Analysis of loading-unloading curves

Careful inspection of loading-unloading curves may provide information about deformation processes in the material during the nanoindentation cycle. The loading-unloading curves obtained with Berkovich as well as cube corner tips were analysed for the Film900.

**Berkovich tip**

Sudden penetrations of the indenter tip at constant load, so called pop-in events, were only occasionally observed at loads of 7000-9000 µN, for low loading rates of \( \leq 45 \) µN/s.

In Figure 5.9 loading-unloading curves with the same maximum load \( P_{\text{max}} = 9000 \) µN, but different loading rates (1800 µN/s and 45 µN/s) are presented. A pop-in event (pointed by an arrow) can only be observed at the lower loading rate.

![Figure 5.9](image)

**Figure 5.9.** Loading-unloading curves corresponding to different loading rates. A pop-in event is only observed at the lower loading rate.

**Cube corner tip**

The appearance of loading-unloading curves is more dependent on the loading rate for a cube corner tip, see Figure 5.10. Loading rate of 300 µN/s results in a fairly smooth loading curve with a small pop-in at \( \sim 1350 \) µN and \( \sim 8 \) nm creep (sinking of the tip into the sample during the holding at \( P_{\text{max}} \)). The curve corresponding to a lower loading rate (75 µN/s) exhibits a “bulge”, i.e. a change in slope, at \( \sim 900 \) µN. This bulge develops to a pop-in when the loading rate is reduced to \( \sim 30 \) µN/s. Almost negligible creep can also be noted. A new
bulge at ~500 µN on the latter curve develops to a pop-in if the loading rate is further reduced to ~26 µN/s.

**Figure 5.10.** Loading-unloading curves obtained with a cube corner tip. The presence of bulges/pop-ins depends on the loading rate.

Loads up to 2000 µN were applied with a cube corner tip. Maximum four pop-in events could be observed at low enough (~15 µN/s) loading rates, see Figure 5.11. The sudden tip penetrations were typically of 2-5 nm.

**Figure 5.11.** Maximum four pop-ins on the loading curve could be observed at low enough loading rate (~15 µN/s).
5.4.2 Analysis of scanning probe microscopy (SPM) images

A great advantage of using Hysitron Triboscope nanoindenter is a possibility to image the surface with an indenter tip (scanning probe microscopy, SPM) before and after making an indent.

SPM images of indents made by Berkovich and cube corner tips are presented in Figure 5.12. Pile-ups are observed in both cases. Note, that the height of the piles, \( h_{\text{pile}} \), is nearly the same: 28 and 26 nm for Berkovich and cube corner tips, respectively, but the applied load differs 10 times (8000 and 800 \( \mu \)N). This indicates that much larger plastic deformation is introduced into the material with a cube corner tip. Piles for a Berkovich tip formed for loads higher than 2500 \( \mu \)N. For a cube corner tip pile formation started at 400 \( \mu \)N.

![Figure 5.12](image)

Figure 5.12. Indents made by a) Berkovich tip (\( P = 8000 \mu \)N, \( h_{\text{pile}} = 28 \) nm) and b) cube corner tip (\( P = 800 \mu \)N, \( h_{\text{pile}} = 26 \) nm).

5.4.3 Deformation mechanism

A cross-sectional TEM image of an indent (\( P_{\text{max}} = 24 \) mN, local film thickness 200 nm) is presented in Figure 5.13.

![Figure 5.13](image)

Figure 5.13. Cross-sectional TEM micrograph of an indent (\( P_{\text{max}} = 24 \) mN).
Maximum and final penetration depths were 187 and 84 nm respectively. Piles of ~52 nm height formed around the indenter tip. No delaminations could be observed, neither along the basal planes, nor at the film/substrate interface. Furthermore, no residual bending of the film/substrate interface has taken place upon indentation, but substantial deformation has been induced in the substrate (1.4 µm in depth).

The TEM images of both piles are shown in Figure 5.14.

![Figure 5.14. TEM images of the a) left and b) right piles; areas indicated by the square boxes are zoomed in c) and d), respectively.](image)

Tilting of the basal planes can be observed in the left pile, see Figure 5.14 a) and c). The boundaries between untilted/tilted (A, C) and tilted/tilted (B) regions are not clear, which indicates that no well defined dislocation walls formed. The buckling of the layers involves ~1/3 of the film thickness, not affecting the ones lying underneath.

The right pile does not have a clear internal structure, no atomic planes can be identified and no kinking indicated, see Figure 5.14 b) and d).
6 Discussion

6.1 Composition

The formation of MAX phases depends strongly on temperature. The growth temperature of 900 °C led to the composition closest to stoichiometric Ti$_2$AlC. Ti$_2$AlC unit cell is quite complex and large, therefore, high atom mobility is required to enable occupation of correct lattice positions. At lower growth temperatures (700 and 800 °C) atom diffusivity is considerably lower and TiC, which has less complicated lattice structure, formation is more favourable.

Al melting temperature is ~660 °C, which, in combination with only minor amounts of Al-containing phase (Ti$_3$AlC) being formed, could lead to Al evaporation at 700 °C and resultant low Al content in the film. Al concentration is, however, higher at increased growth temperatures due to formation of Ti$_2$AlC, i.e., Al atoms are bound in the lattice.

High O incorporation in the structure has been detected, in agreement with the results reported by Rosén et al.[5] Most likely, this O originates from the substrate and residual gas (water vapour), possible sources being water inclusions in porous graphite cathode and water desorbed from the vacuum chamber walls upon heating. The O content was independent on the growth temperature. The H concentration, however, was below the detection limit, possibly due to ion induced formation of H$_2$ with subsequent removal.[25] Correspondingly, formation of O$_2$ molecules does not take place, possibly because the O-O bond is weaker than the Ti-O bond, and therefore O uptake by the lattice is more favourable.[26]

6.2 Structure

Films grown at low temperatures are often composed of grains and exhibit low structural quality. Impurity atoms tend to accommodate along grain boundaries, occupy vacancy positions or interstitial/substitutional sites in the structure. High O incorporation at 700-800 °C is therefore not unexpected.

Presence of O in (close to) single crystalline Ti$_2$AlC is, however, less expected. The weak correlation between the C and O concentration as shown in the ERDA composition profile for the Film900, suggests substitutional O in C lattice sites, in agreement with the results published by Rosén et al.[5] In the Film900, C and O concentrations together correspond to ~26 at.%, which is approximately the C content in pure Ti$_2$AlC. Substitutional O is also supported by the fact that C in Ti$_2$AlC is only bonded to Ti, while Ti has high chemical affinity to O. Furthermore, C and O atoms are similar in size (both have covalent radii of 68 pm).[27]

Ti$_2$AlC with high substitutional O content in the structure is comparable to metallic oxycarbides (MC$_x$O$_y$, M – early transition metal). It has been demonstrated that for M = Ti, O can replace C over a wide range of concentrations.[28] However, it is unlikely that all C in the MAX phase structure can be substituted by O, since O atoms tend to interact strongly with each other, possibly initiating MAX phase decomposition to more energetically favourable phases.
Due to similar size of C and O atoms, the substitution does not introduce stress fields which could induce local phase transformations or formation of grains. The characteristic nanolaminated MAX phase structure is therefore retained.

6.3 Mechanical properties

6.3.1 Hardness

A hardness of 16 GPa has been measured for the arc deposited Ti$_2$AlC thin film. The dependence of mean pressure, $p_m$, vs. maximum penetration depth, $h_{max}$, exhibited a clear plateau followed by increased $p_m$ values for increased indentation depth, due to the Al$_2$O$_3$ substrate influence (see Figure 5.5). In contrast, for magnetron sputtered Ti$_2$AlC thin films, the hardness decreased with increased indentation depth, as observed by Wilhelmsson et al.\cite{14} Two Ti$_2$AlC thin film hardness values were therefore reported: 20±1 GPa for shallow ($h_c < 120$ nm, i.e., 20 % film thickness) and ~15 GPa for deeper indents. The same effect has previously been indicated in Ti$_3$SiC$_2$ MAX phase,\cite{17} where hardness reduction was ascribed to formation of kink bands and delamination of the basal planes. This implies that less severe deformation takes place upon indentation of Ti$_2$AlC films investigated in this Thesis.

The different behaviour could be determined by film quality, as resulting from the growth method and impurity incorporation. For example, it has been observed that arc deposited thin films in some cases exhibit lower residual stress than magnetron sputtered ones, which could possibly explain that the Ti$_2$AlC films grown by cathodic arc exhibited lower hardness compared to the value for shallow indents in magnetron sputtered Ti$_2$AlC. However, most likely of higher importance is defect density and crystal quality, since the sputtered films were reported to contain regions of a cubic phase intergrown in the MAX phase layer.\cite{14}

Ti$_2$AlC thin film investigated in this Thesis was characterized by high O content, while magnetron sputtered Ti$_2$AlC films were relatively pure (below XPS detection limit) from contaminants. At present, it is difficult to predict O influence on mechanical properties of Ti$_2$AlC. As indicated, O replaces C, i.e., a fraction of the Ti-C bonds are replaced by stronger Ti-O bonds. However, it does not necessarily mean that the structure becomes harder and stiffer – the deformation may still be mainly absorbed by weaker Ti-Al bonds (a good analogy is springs connected in series).

6.3.2 Elastic modulus

Reduced elastic modulus extrapolated to zero depth $E_{r0}$ of 223 GPa (which corresponds to $E = 259$ GPa) was determined for the Film900. $E_r$ increased linearly with increased penetration depth due to the substrate influence. In analogy to H, a decrease of $E_r$ with increased penetration depth was observed for magnetron sputtered Ti$_2$AlC: nearly constant $E_r$ of 260±10 GPa was reported for shallow ($h_c < 120$ nm, i.e., 20 % film thickness) and ~240 GPa for deeper indents \cite{14}. For comparison, in the $h_c$ interval of 25-71 nm corresponding to 5-9 % film thickness, $E_r$ of the Film900 increased from 246 to 303 GPa.

Elastic modulus of the Film900 obtained with a Berkovich and cube corner tip were 259 GPa and 214 GPa, respectively. The discrepancy could be ascribed to cracking and
delaminations, more easily induced with a cube corner tip. In case of strain relaxation via cracking/delamination, nanoindenter suddenly penetrates into the sample which is equivalent to less “support” from the material and in calculations results as lower E (and H) value. Although no surface cracks were observed in the SPM images, presence of internal cracks or delaminations of basal planes is very likely, as supported by observation of pop-in events.

Elastic modulus values obtained with a cube corner tip increase with increased TiC content in the film, i.e., $E_{\text{Film900}} < E_{\text{Film800}} < E_{\text{Film700}}$ (214 GPa < 259 GPa < 282 GPa), which is expected, as elastic modulus for TiC is higher (~450 GPa) than for Ti$_2$AlC. Higher concentration of point defects at lower growth temperatures may also have a certain effect.

It should be noted that Ti$_2$AlC exhibits large E/H ratio (16.3), which is more typical for ductile metals than for brittle ceramics.

### 6.3.3 Materials deformation

Upon indentation with a Berkovich tip, pop-ins in loading-unloading curves are exhibited at maximum loads $\geq 300$ µN [17] and $\geq 7000$ µN for Ti$_3$SiC$_2$ and Ti$_2$AlC, respectively. For a cube corner tip, the first pop-in appears already at $\sim 50$ µN for Ti$_3$SiC$_2$ [17] while to induce a pop-in in Ti$_2$AlC $\sim 500$ µN are required. A cube corner tip creates more plastic deformation, i.e., dislocations, as compared to a Berkovich tip at the same load. Pop-in events are thus exhibited at lower loads.

According to Molina et al., pop-in events in MAX phases are related to kinking accompanied by delaminations of the basal planes. However, in the study of the deformation behaviour of Ti$_3$AlC$_2$, TEM images demonstrating kink bands correspond to maximum load of 30 - 40 mN [10] while pop-in events in loading-unloading curves appear from 300 µN [17]. It is not clear, if such low loads are enough to initiate kinking. Another explanation of pop-ins in MAX phases could be relaxation of strain, as is also observed in other materials, e.g. alumina.

A weak indication of kink band formation and no delaminations have been observed in TEM images of the Ti$_2$AlC film investigated in this Thesis. The data points of loading-unloading curve of the indent were too scarce to identify eventual pop-ins.

Presence of pop-ins and amount of creep depends strongly on the loading rate. This can be understood by considering dislocation motion: dislocations are created upon loading and move under the influence of strains. If the loading is fast, elastic strain relaxation occurs mainly during the holding at the maximum load $P_{\text{max}}$, which leads to high creeping effect. On the contrary, if the indenter tip is pressed into material slowly, dislocations move already during the loading and eventually collapse, which results as one or several pop-in events. The creeping is considerably reduced.

It has also been suggested that kink bands explain large pile-ups around the residual indent [10]. In this study, however, presence of pile-ups could not be unambiguously related to pop-in events: pile-ups were observed at $P_{\text{max}} \geq 3000$ µN while pop-ins only occasionally appeared at $P_{\text{max}} \geq 7000$ µN for a Berkovich tip. This implies that there may exist other
mechanisms than kinking behind the formation of pile-ups in MAX phases. This is also confirmed by the TEM results.

Cross-section of an indent was investigated by TEM to get an insight into the single crystalline Ti$_2$AlC thin film deformation mechanism upon nanoindentation. According to Zhou et al.[11] and Molina et al.[10] formation of kink bands and delamination of basal planes could be expected as energy releasing mechanisms. However, no well defined kink bands were observed in the TEM image. Several possible reasons are discussed below.

1) Film thickness

There may exist a critical thickness, which must be exceeded to allow layers to buckle effectively. Free surface is created upon penetration of a nanoindenter tip into material. The free surface energy must be counterbalanced by the volume energy. A thick film allows deep indents to be made, i.e., large change in the volume energy, which means that cracking and delamination can be initiated. Delamination is closely related to kink formation. If a film is too thin, not enough energy to drive kinking is provided with a shallow indent and material is displaced via flow.

2) Load not high enough

It is reasonable that critical $P_{\text{max}}$ to create a kink band exists. A lower load may be not enough to break the atomic layers. The critical $P_{\text{max}}$ may also depend on the film thickness.

3) Loading rate too fast

Analysis of loading-unloading curves showed that loading rate strongly affects the way the material deforms. The indent for the cross section analysis was made with a Berkovich tip pressed into the material at the rate of ~400 $\mu$N/s. As has been discussed, in case of high loading rate elastic strains do not have enough time to relax during the loading phase. Also, a creep effect can not be evaluated since holding at $P_{\text{max}}$ was not included in the loading profile.

Dislocations moved mainly during the unloading phase. The continuously reduced load could affect the dislocation motion before a full strain relaxation has occurred, i.e., “freezing” a kink band in an early formation phase (as possibly is observed in the left pile).

4) Substrate effect

The film is deposited on a hard (H = ~30 GPa) and stiff (E = ~500 GPa) Al$_2$O$_3$ substrate which does not deform easily. At high loads, the film material displaced by the nanoindenter tip may be “reflected” from the substrate-film interface and pushed back. Dislocations on other planes than the basal ones may become mobile, and the condition of dislocation mobility on the basal planes only is then not fulfilled. Thus, deformation via kinking is prevented.

5) Oxygen

Substitutional O in C sites should not have an influence on the deformation if only dislocations on the basal planes are activated (under the assumption that weak Ti-Al bonds
only are broken as dislocations move). However, if some of the O atoms occupy interstitial positions near the basal planes, then dislocation motion on the basal planes may be hindered, other dislocation glide systems become favourable, and kink band formation prevented.

Interstitial O is, however, not expected, as no corresponding Al-O vibrations have been observed in FTIR spectra.[5]
7 Conclusions

Composition, structure and mechanical properties of arc deposited Ti-Al-C thin films were investigated in this Thesis. Accommodation of significant amount (7-12 at.%) of oxygen was confirmed, evidently not destroying the characteristic nanolaminated structure upon MAX phase formation. Hardness and elastic modulus of 16 and 259 GPa, respectively, was determined for the Ti$_2$AlC film deposited at 900 °C.

Analysis of loading-unloading curves and SPM images revealed no relation between pop-in events and presence of pile-ups. This implies that another mechanism than formation of kink bands may stand behind the formation of pile-ups. Supporting this, no clear formation of kink bands have been observed in TEM images, possible reasons being too thin film, too low load, too fast loading rate, substrate effect or high oxygen content. Large pile-ups formed via material flow.
8 Future work

The work presented in this Thesis is one of the first attempts to investigate the influence of impurities on MAX phase properties. More experiments must be performed in order to understand the correlation impurity-property and achieve full control in the production of films with desired characteristics.

The oxygen content in Ti$_2$AlC should be changed in a controllable way to determine the maximum oxygen concentration which does not destroy the characteristic nanolaminated MAX phase structure. Resulting effects on the material properties is then of interest, indicating over what range the properties can be tuned. Other elements as predicted by atomistic simulations should also be attempted to be introduced into the lattice, in combination with growth of other promising MAX phases.

Films with different oxygen content should be investigated by nanoindentation to determine elastic modulus and hardness dependence on oxygen concentration. Thicker films (≥ 500 nm) should be grown at 700 and 800 °C to allow measurements with a Berkovich tip. Other properties (e.g., electrical resistivity, thermal stability, friction coefficient) of “oxygen-rich” Ti$_2$AlC should also be studied.

Series of indents with different maximum loads and loading rates should be analyzed by cross sectional TEM to understand deformation dependence on the loading conditions. Indents should be made into both “oxygen-rich” and “oxygen-free” films to investigate oxygen influence on the deformation behaviour.
References


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